SCIENCE FOR GLASS PRODUCTION

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HEAT-ABSORBING GLASS: DIRECTIONS OF SYNTHESIS

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The process of producing light- and heat-absorbing glass of a wide color range is considered. The scheme of reactions of various color centers related to Se, CoO, FeO, Fe_2O, and combinations of them is described. The results obtained can be used in production of household, container, light engineering, and other types of glass.

The methods for achieving a particular tint shade in glass are of special importance for practical glass melting, and using single pigments is less common than using colorant mixtures.

Mixing of colorants is a substractive process implemented in a way that makes the tint generated by these colorants as complementary as possible to the existing glass tint. A third colorant is used as a corrective, so that the final coloring would be maximally neutral [1].

A combination of three colorants (iron powder – selenium – cobalt oxide) ensures good results in coloring reproducibility.

Let us analyze separately each component of this combination.

Iron is an ionic colorant that is present in glass in two degrees of oxidation (Fe^{2+} and Fe^{3+}). The degree of iron oxidation depends on the melting conditions. Thus, Fe^{2+} predominants in glasses melted under reducing conditions. Their spectral curves have absorption bands at a wavelength of 0.48, 0.63, 0.71, and 1.10 μm. The glass has a bluish-green tint.

If the glass is melted under oxidizing conditions, Fe^{3+} predominants in it. The spectral curve exhibits absorption bands in the purple and red spectral ranges with transmission maximum in the region of 0.55 μm. The glass has a yellowish-green tint.

These glasses have more intense absorption in the UV spectral range than glass with Fe^{2+}. The situation in the IR range is the opposite: the higher the Fe^{3+} content, the less intense the absorption [1 – 3].

Selenium is a molecular colorant. It resembles sulfur in its properties; however, it is more electropositive and can be retained in glass in its elemental form in melting under moderately oxidizing or neutral conditions [1]. It exists in glass in the form of Se^{2-}, i.e., selenides and polyselenides, and Se^{4+}, i.e., colorless selenite.

Selenides and polyselenides of alkali and alkali-earth metals are colorless or impart a light yellowish-brown tint to glass, whereas selenides of heavy metals impart intense brown (FeSe, Fe_2O_2Se) and black (CoSe) colors to the glass melt [4].

However, under highly oxidizing conditions, the prevailing components are selenates (Se^{6+}), which do not tint glass.

Selenium atoms produce two absorption peaks in the visible spectral range (0.50 and 0.75 μm), i.e., in the red range of the spectrum. With increasing temperature the absorption bands broaden and shift in the longwave direction.

Under highly reducing glass-melting conditions, evaporation of selenium from the melt decreases significantly, but the element exists in the form of selenides producing undesirable coloring.

The loss of selenium through evaporation under neutral and weakly oxidizing melting conditions comprises 70 – 80% of the quantity introduced [5].

Moderate oxidizing conditions in melting are usually achieved by adding saltpeter and sodium sulfate to the glass batch. However, a large dose of sodium sulfate can weaken the tinting due to oxidation of selenium to selenite.

The sulfate foam appearing fosters significant volatilization of selenium, which easily dissolves in this foam.

The batch should also contain the minimum admissible quantity of saltpeter ($NaNO_3$) to ensure formation of sodium selenates and prevent substantial oxidation of iron to Fe^{3+}.

Solid-phase and liquid-phase reactions between selenium and saltpeter result in formation of sodium selenites and

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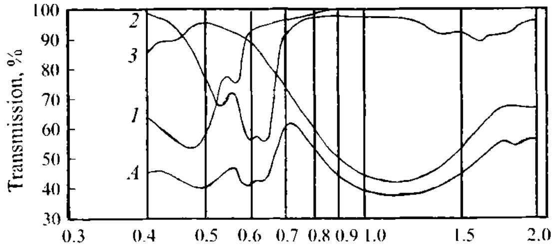

Fig. 1. Spectral transmission of glasses containing selenium (*1*), cobalt (*2*), and iron (*3*): *A*) overall light-transmission curve representing the combined effect of the three coloring agents.

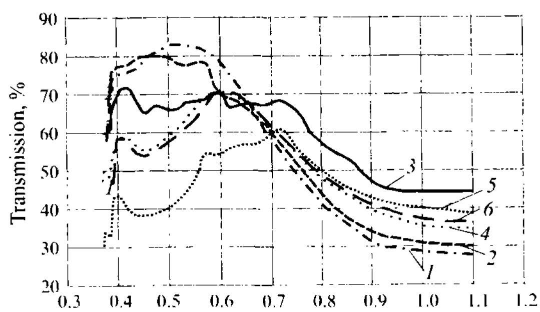

Fig. 2. Spectral transmission curves of LHA glasses: *1*) green-sky-blue; *2*) sky-blue; *3*) gray; *4*) bronze; *5*) dark bronze; *6*) amber.

selenates, which dissolve in the glass melt and impart to the glass melt a pink shade caused by selenium ions.

Thus, when selenium is used, the glass melt is physically decolorized, and two complementary colors (yellow-green from Fe^{3+} and pink from selenium) in combination produce a gray tone.

A yellow color in glass has to be removed by small cobalt additives [1].

Cobalt is the most common ionic colorant in glass melting. It forms three oxides: CoO, Co_3O_4, and Co_2O_3. Under reducing or oxidizing melting conditions cobalt is present in the glass melt only in the bivalent form, since the tri- and tetravalent forms are instable at melting temperatures:

$$Co_3O_4 \rightarrow 3CoO + \frac{1}{2}O_2;$$

$$Co_2O_3 \rightarrow 2CoO + \frac{1}{2}O_2;$$

$$CoO + Co_2O_3 \rightarrow 3CoO + \frac{1}{2}O_2.$$

Cobalt-tinted glasses transmit purple and blue rays and extreme red rays well, and therefore they have a blue or purple color.

The absorption in the orange, yellow, and green spectral ranges is intense. All curves show three clearly defined maxima, the two highest of which (0.60 and 0.65 μm) are stable, and their position does not change under changes in the composition of the principal glass. The third maximum (0.545 μm) can shift up to 0.505 μm, depending on the glass composition. The presence of cobalt does not have a perceptible effect on light transmission in the UV range.

Absorption bands are clearly recorded near the infrared range at a wavelength of 1.25 and 1.75 μm.

Cobalt tinting is technologically stable and does not depend on the melting conditions.

Figure 1 shows spectral curves of glasses with selenium, cobalt, and iron.

Using iron oxide alone introduced into the batch in the form of ferrous powder or oxide (crocus) makes it possible to obtain light- and heat-absorbing (LHA) glass with high transmission of bluish-green or green color. When cobalt oxide is added to it, the resulting glass has a light-blue tint of neutral low color purity, which does not distort the chromaticity of objects viewed through this glass. Low color purity is one of the main requirements imposed on all types of LHA glasses.

The combination of a relatively high iron content and a small quantity of metallic selenium (without cobalt) added to the batch imparts an amber (grayish-yellow) tint to the LHA glass. When all three absorbing components (iron, cobalt, and selenium) are simultaneously introduced, depending on their concentration, one can obtain LHA glasses with rather high light transmission, good thermal protection from solar radiation, and neutrally gray, bronze, or a transitional grayish-bronze color or dark-colored glasses with saturated gray and bronze colors and decreased transmission in the visible and IR spectral range (up to 50 and 45%, respectively).

Besides LHA glasses with a wide color range (from sky-blue to dark bronze), the specified additives can be used to produce tinted glass without heat-absorbing properties. Such glasses can be used as glass furniture components and decorative mirrors and in interior decoration. An increased concentration of metallic selenium introduced into the batch with a small additive of iron (or ferric oxide) makes it possible to produce "rosalite," which is glass with a pink shade.

Combinations of selenium with cobalt oxide in various concentrations impart lilac, purple, and gray color shades to glasses. Figure 2 shows spectral curves of LHA glasses of a wide color range with different combinations of colorant additives.

Thus, based on published and experimental data, the process of producing LHA glass of a particular color tint can be represented as a scheme of interaction of different color centers related to Se, CoO, FeO, Fe_2O_3, and their combinations Fe_2O_2Se, CoSe (Fig. 3).

Thus, the amber tint in LHA glass is related to the pink color center (PCC) of selenium and the yellow color center (YCC) of Fe_2O_2Se, i.e., it is necessary to develop technological conditions for some of the selenium to form its own PCC

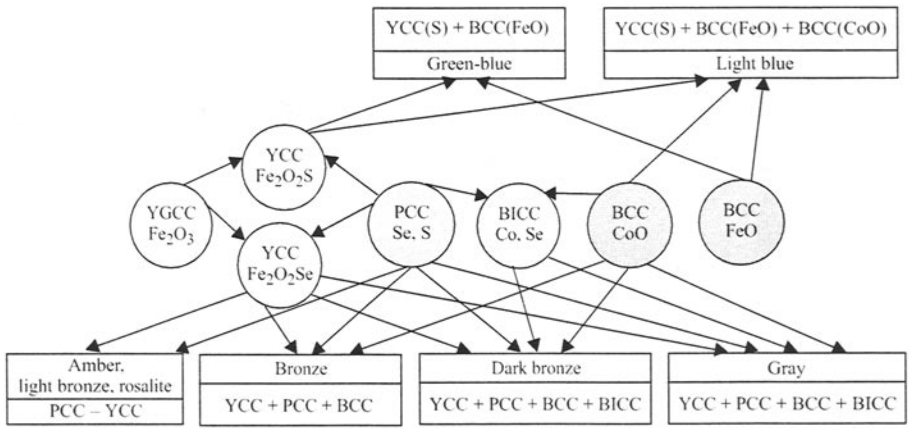

Fig. 3. Scheme of interaction of various color centers.

and the other part to be spent on converting the yellow-green color center (YGCC) of Fe_2O_3 to the YCC (Fe_2O_2Se).

The bronze tint in glass is related to the PCC (Se), YCC (Fe_2O_3Se), and blue color center (BCC) (CoO), i.e., some of the selenium forms its own PCC, and the other part converts the YGCC to the YCC. The BCC imparts a neutral tone.

With increasing amount of CoO, conditions are created for formation of stable black color centers (BlCC) in addition to BCC, which makes it possible to produce LHA glass of a dark bronze tint.

The basic composition of the glass and the batch, the type, concentration, and ratios of the colorant additives, glass-melt clarifiers, and melting catalysts, the batch preparation cyclogram, the time and temperature conditions for melting, the redox potential of the glass melt, the gas medium in the melting furnace are the main factors that determine the technological properties and color of the produced glass melt.

In production of LHA glasses of a prescribed color shade the developed scheme can be used to create conditions for intended formation of the needed color centers.

The proposed scheme can be also used in production of household, container, illumination, and other types of glasses.

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